Energy Conservation in Ceramic Giftware Using Canadian Minerals and Raw Materials

FINAL REPORT

by

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SUMMARY

The first phase of a program initiated to develop single fired decorative ceramic giftware has been completed. The results obtained during this phase are reported herein as the final report for the project entitled "Energy Conservation In Ceramic Giftware Manufacture Using Canadian Industrial Minerals and Raw Materials". The completion of this project was made possible through the funding of The Department of Energy, Mines and Resources under the contract DSS File No. 14SQ.23440-3-9012.

The project was undertaken by Blue Mountain Pottery Limited to identify suitable ceramic body formulations with low firing temperatures in the firing range of decorative ceramic decals (750-850^{o}C). The Ontario Research Foundation was subcontracted to perform the laboratory development of such bodies under the supervision of Blue Mountain Pottery.

Under this phase of the project body compositions based on local clay raw materials, with minor additions of either glass cullet or a commercial glass frit, have been identified which successfully fulfilled the project objective. In addition, a similar clay based formulation containing zinc oxide and titanium dioxide was identified which produced a much lighter coloured body than the conventional Blue Mountain body. It is anticipated that these bodies could form the basis of a new "Terra Cotta" product line which is foreseen to have a substantial export market in both Japan and the United States. Four of the most promising candidate body formulations are presented in Table 1 (page 3).

Due to the successful completion of this phase of the program it is recommended that the project be continued into the second phase. In this phase the necessary technology required for the commercial production of the single fired "Terra Cotta" giftware will be developed to a pilot level based on the aforementioned body formulations.

1. INTRODUCTION

Currently the manufacturing of decorative ceramic giftware at Blue Mountain Pottery Limited requires that each ite e fired at least twice and for a large number of items three firings are necessary. Initially the ceramic body is fired to the bisque to which, after cooling, a glaze slip is applied and the piece refired. In some cases a decorative decal is applied and the piece fired for the third time to the curing temperature of the decal. Decorative giftware that requires only one firing to obtain the final product could be produced at much lower costs to the Company due to the reduced energy requirements as well as lower number of manhours spent in handling each piece between firings.

In April, 1983, a project was initiated by Blue Mountain Pottery Limited, in conjunction with the Ontario Research Foundation, to identify ceramic body formulations which could be fired at the low temperatures (750-850^{o}C) required for the curing of decorative decals. The development of such a body would permit the application of a decal to the green body which could then be fired to maturity in a single step without overfiring the decal.

This report summarizes the accomplishments of the first phase of the development of single-fired ceramic giftware. The details of the experimental results are presented in the ORF final report attached as Appendix A.

2. OBJECTIVES

The overall objective of this project is: to develop decorative ceramic giftware which can be produced with only one firing cycle.

The objective of the first phase of the project to which this report applies was: to conduct research on a laboratory scale into ceramic body formulations based on Canadian raw materials which can be fired at the low temperatures required for the curing of decorative decals.

3. MAJOR ACHIEVEMENTS

Under this phase of the program research was concentrated on identifying materials which could be substituted into a clay body as fluxing agents to lower the firing temperature of the body to the desired range. The clay body formulations were based on the clays currently utilized at Blue Mountain which are normally fired to 1050°C.

The major achievements accomplished throughout the course of the experimental work are listed as follows:

(i) Body formulations containing the addition of 20% glass cullet (-150 mesh) or commercial glass frit (Ferro frit 3110) produced a well fired clay body at temperatures as low as 840°C.

(ii) Specimens from the batches containing 20% glass cullet or Ferro frit #3110 had higher strengths and lower moisture absorption when fired at 850°C than the existing Blue Mountain pressing body when fired at 1050°C.

(iii) The addition of 10% (dry weight) zinc oxide to the body formulation caused a change in the colour of the fired body from terra cotta to a light tan colour. Further lightening of the tan colour was produced with the addition of titanium dioxide at a 10% level.

(iv) Four body formulations which were considered to be promising candidates for further development work were identified. These formulations are presented in Table 1.

TABLE 1

Most Promising Formulations of Bodies for Single-Fired Ware

Materials	Weight % SF16	SF17	SF25	SF20
Red shale	40	40	35	40
Blue shale	40	40	35	40
Glass cullet	20	-	20	-
Ferro Frit 3110	-	20	-	-
Zinc Oxide	-	-	10	10
Titanium dioxide	-	-	-	10

(v) Successful in-plant trials were performed at Blue Mountain in which an experimental batch prepared with 10% zinc oxide added to the existing slip casting body was cast into shapes, decals applied to the greenware and the ware fired at 1050°C. Additional trials were successfully performed in which a transparent glaze was sprayed onto the greenware and the decals applied onto the glaze. The pieces were then fired in a single firing cycle.

4. PROGRAM PROGRESS

4.1 Identification of Body Formulations with Suitable Firing Parameters

The experimental work was carried out at the Ontario Research Foundation. The details of this work are presented in the final report prepared by ORF attached as Appendix A.

Body formulations investigated were based on the existing clays used at Blue Mountain which included red, blue and green shales from the Collingwood and Meaford areas. A number of body fluxing agents were

individually substituted into the clay bodies and samples qualitatively evaluated with respect to firing temperature in gradient firing trials. Candidate materials included: flyash
silica fume
nepheline syenite
spodumene
petalite
iron oxide (pigment grade)
glass cullet (-150 mesh)
glass frit (Ferro 3110)
zinc oxide

Normal addition levels were between 10 and 20 per cent.

The greatest reduction in firing temperature was provided by glass cullet and the Ferro glass frit. Firing temperatures were observed as low as 840°C for batches prepared with 20% additions of either material. Also during these trials it was found that the normal terra cotta colour of the clay body could be altered. The addition of zinc oxide at a 10% level produced a light tan coloured body between 875°C and 1025°C. The further addition of 10% titanium dioxide resulted in an even lighter coloured body over a broader temperature range of 825 to 1060°C in batch SF20.

Selected body formulations were evaluated with respect to strength, moisture absorption, shrinkage and shape retention when fired at temperatures of 850, 950 and 1050°C. The values for these properties for three of the most promising batches fired at 850°C are compared to the properties of the existing Blue Mountain pressing body prepared under similar conditions in Table 2.

TABLE 2

Physical Properties of Test Batches Fired to 850°C

Batch	Fired Strength MOR (psi)	Moisture Absorption(%)	Linear Shrinkage (%)
*SF16-20% glass cullet	4053 ± 241	8.9	2.01
*SF17-20% Ferro 3110	3807 ± 281	4.8	2.16
*SF25-20% glass cullet 10% ZnO	3154 ± 342	9.5	1.80
B.M. Body-fired 850°C	2108 ± 426	15.8	0.21
B.M. Body-fired 1050°C	3882 ± 330	12.3	0.95

* Note: Specimens fired at 850°C.

The fired strengths of each of these trial batches was improved over that of the current Blue Mountain body fired at 850°C and in batches SF16 and SF17 the strengths were greater than or equivalent to that of the Blue Mountain body fired at 1050°C. The moisture absorption of each of the trial batches was reduced in comparison to the Blue Mountain body fired at either 850 or 1050°C. The fired shrinkage of each of the trial batches was higher than the Blue Mountain body which may be due in part to the presence of wollastonite in the Blue Mountain body since wollastonite will reduce fired shrinkage.

4.2 In-Plant Firing Trials of Decalled Greenware

Trials were performed at Blue Mountain with an experimental batch which involved the casting of the body, decal application to the greenware and firing the pieces in one firing cycle.

The formulation of the batch was similar to the existing Blue Mountain slip casting body only 10% zinc oxide had been added. Ten kilograms of the production slip casting slurry was mixed with 600 grams of

*zinc oxide in a ball mill for 1/2 hour. The specific gravity of the slip was adjusted to 1.85 with the addition of water. The slip was cast in a test mould which produced flat surfaced pieces as illustrated in Figure 1. No problems were encountered in the casting of the pieces.

Experimental ceramic decals were obtained from Commercial Decal of New York which were referred to as "raw glaze decals" and were supplied with a special application medium. The decals were applied following the manufacturer's instructions. Photographs of the decals used are presented in Figures 2 and 3. These particular decals require firing near 1050°C.

A total of 12 pieces were cast from the trial batch. Two sets of trials were performed with 6 pieces for each set. In the first set the decals were applied to the greenware and the pieces fired to 1050°C. In the second set a transparent glaze was sprayed over the top surface of the unfired piece and the decals were applied over the glaze. The transparent glaze used was a production glaze, N.G. Clear Glaze. The glaze formulation is:

60%	lead bisilicate
26.5%	borax
13.5%	Edgar Plastic Koalin

In the first set of firing trials the decalled greenware was fired successfully with no problems due to gas bubbles or separation of the decal from the piece being observed. However, the quality of the fired pieces was less than satisfactory. It was found that some of the coloured areas of the decals would dust off from the surface of the ware when brushed with a finger tip leaving only the underlying outline of the decal pattern. The colouring oxides had not fused to the body. This was especially noted with Decal #1. In Decal #2, the dusting problem was less severe but the decal background around the floral pattern was very noticeable after firing as can be seen in Figure 4. The colour of the body fired to 1050°C was a pleasant sand colour.

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* Zinc Oxide used was a commercial grade supplied by the Pigment and Chemicals Co., Milton, Ontario.

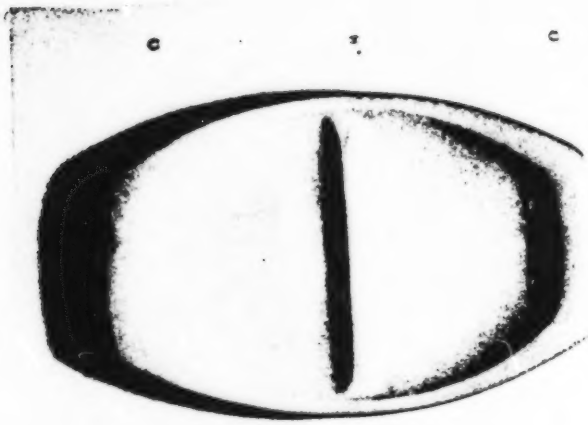

Figure 1
Sip Cast Tray from Plant Trials

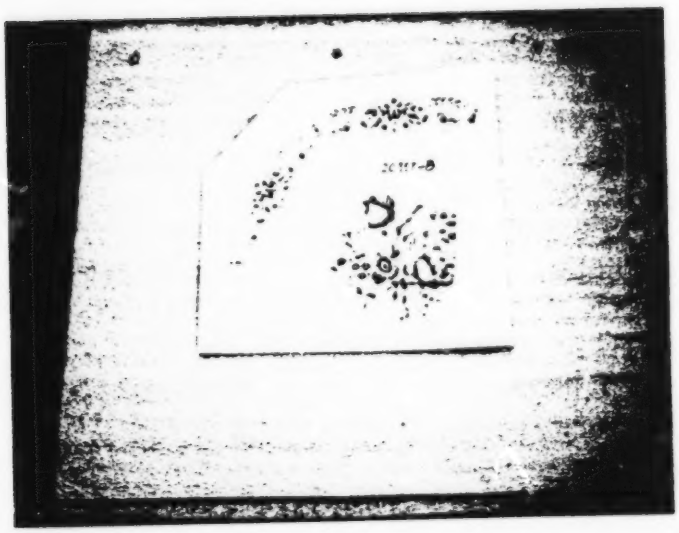

Figure 2
Experimental Decal #1
from Commercial Decal

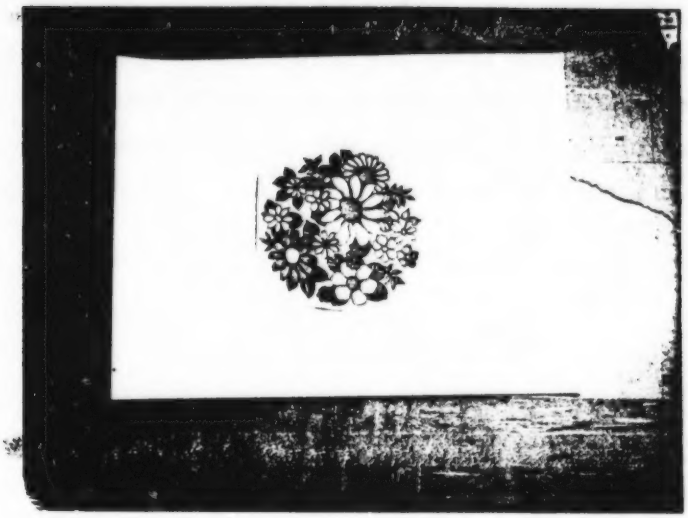

Figure 3
Experimental Decal #2 from Commercial Decal

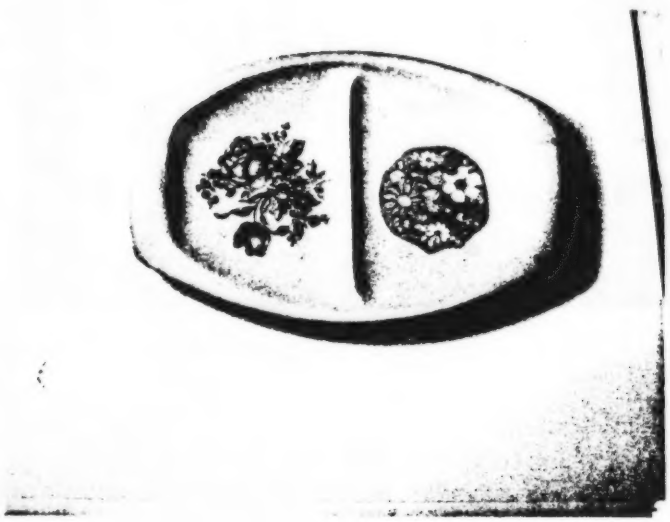

Figure 4

Single-Fired Decalled Ware
-Note the decal background showing around the floral patterns of Decal #2 on the right side.

In the second series of trials again no problems were encountered in firing the glazed, decalled greenware. The quality of the surface of the piece proved to be much better as the colours of the decal had fused into the molten glaze during firing. Also the decal background was unnoticeable in Decal #2. The colour of the glazed pieces was found to be darker as a result of the transparent glaze. Photographs of an unglazed piece and glazed piece both fired to 1050^{o}C are presented in Figure 5.

Fig.5
Photograph of Piece Decalled, Glazed and Fired with a Single Firing
- Note darker appearance of glazed piece

An additional experimental batch, SF17, was prepared at ORF for pressing trials. However, it was found that the supplied batch was much too stiff to complete these trials without resulting in damage to the pressing moulds. The moisture content of the supplied batch was found to be too low at approximately 14.5% and was returned to ORF for water addition. (A moisture content of 20-21% is maintained in the existing pressing body). After reworking, the batch was again delivered to Blue Mountain but again the batch was too stiff with a moisture content of ~15.5%. Therefore the pressing trials with this batch were not performed.

5. CONCLUSIONS AND RECOMMENDATIONS

From the results obtained throughout the experimental work performed at ORF it can be concluded that a ceramic body fired at 850°C with a lower moisture absorption and strength equivalent to or greater than the existing Blue Mountain body fired at 1050°C, can be produced with the addition of either 20% glass cullet or the commercial glass frit, Ferro 3110. These body formulations have firing temperatures in the desired 750-850°C curing range of the ceramic decals currently used in production at Blue Mountain and based on this property would be candidate bodies for the production of single-fired decalled giftware. Due to the complications encountered in the pressing trials of batch SF17 it is recommended that further development of the body formulations identified at ORF be performed in order to optimize the overall properties of the bodies. It may be necessary to reduce the glass levels to improve the plasticity of the body.

It can also be concluded that the addition of zinc oxide to body formulations based on the existing Blue Mountain clays will produce of lightening of the colour of the body to a pleasant tan or sand colour. Further lightening of the colour can be accomplished with the addition of titanium dioxide.

Based upon the results of the plant trials it appears feasible to fire decalled greenware in one cycle with no problems due to gas formation under the decal. The only major problem that was observed was the incomplete fusion of the decal coloured zones to the body resulting in

dusting of the colours. (This was found to be remedied by applying the decal onto a thin layer of glaze sprayed over the greenware surface prior to firing). The single firing of glazed decalled greenware also appears to be feasible based upon the results of the plant trials. The best method for glaze application would be spraying to ensure that the greenware does not absorb too much water. The current glazing procedure of dipping used at Blue Mountain would not be suitable for greenware. Further improvements in the fusing of the decals to the body may be accomplished if fluxing agents were incorporated between the body and decals.

Finally, in order to develop the single-fired decorative giftware to a commercial production scale it is recommended that Phase II of the program be initiated.

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President

M. Kapadia

APPENDIX A

Report No. 67065-83-4

Blue Mountain Single Firing

for

Blue Mountain Pottery Limited
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Attention: Mr. R.W. Miller

FINAL REPORT

Period Covered: April 20 - August 31, 1983
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1. INTRODUCTION

In April, 1983, the Ontario Research Foundation (ORF) was subcontracted by Blue Mountain Pottery Ltd to conduct research into ceramic body formulations which could be fired at the low temperatures (750 to 850°C) required for the curing of decorative ceramic decals. The development of such a body would enable Blue Mountain to apply decals to greenware and fire simultaneously without the risk of overfiring the decal, thus eliminating a firing cycle from the normal production process. This project has been successfully completed as the first phase of a program initiated by Blue Mountain to develop decorative ceramic giftware which can be produced with only one firing cycle.

Body formulations have been identified which could be fired to temperatures as low as 840°C. Formulations containing 20% (dry weight basis) levels of glassy materials and fired at 850°C were found to display improved physical properties over the existing Blue Mountain body fired at 1050°C. An additional development established under this project was the ability to alter the normal terra cotta colour of the existing body to an aesthetically pleasing tan colour through additions of zinc oxide and titanium dioxide to the body formulation.

This report describes the experimental work carried out by ORF to accomplish the above objective of Phase 1 of this project.

2. BODY DEVELOPMENT

2.1 Raw Materials Selection

The existing clays used by Blue Mountain Pottery were chosen as the base materials of the body. These clays are identified as red, blue and green clay which are in actuality similar in nature as they all originate from similar glacial deposits known as the Meaford and Dundas shale deposits.

Blue Mountain utilizes two different body formulations in their production process. Separate formulations are prepared for slip casting and ram pressing. These formulations are listed as follows:

(i) Slip Casting Body

	parts by weight
red clay	53.7
green clay	25.4
blue clay	7.5
Wollastonite	10.0
nepheline syenite (A270)	3.5
soda ash	0.16
sodium silicate	0.08

(ii) Pressing Body

	parts by weight
red clay	43.5
blue clay	43.5
Wollastonite	10.0
nepheline syenite (A270)	3.0
$BaCO_3$	0.5

Batches with formulations representative of the Blue Mountain bodies were selected as reference batches for all further work.

The typical firing temperature for the Blue Mountain bodies is 1,050°C. Under this project it was desired to reduce the firing temperature to between 750 and 850°C. In order to achieve this a number of materials were selected as potential body fluxing agents which could be substituted into the body formulation. The candidate materials included:

(i) flyash
(ii) silica fume
(iii) nepheline syenite
(iv) spodumene
(v) petalite
(vi) iron oxide
(vii) glass cullet
(viii) commercial glass frit
(ix) zinc oxide

(i) Flyash: flyash is a residual waste material recovered from the burning of coal in electrical power plants. Much of the ash is in the form of glassy beads mixed with crystalline species. The major components are SiO_2, Al_2O_3 and Fe_2O_3. The flyash used in these trials originated from the Lakeview power plant in Mississauga, Ontario.

(ii) Silica fume :

silica fume is a byproduct resulting from the reduction of high purity quartz with coal in electric arc furnaces during the manufacture of ferrosilicon and silicon metal. The fume consists of very fine particles of approximately 90% amorphous silica.

The source of the silica fume was S.K.W. in Becancour, Quebec.

(iii) Nepheline syenite :

a granular igneous rock made up of nepheline, potash feldspar, soda feldspar and minor minerals such as mica, hornblende and magnetite. Two grades of this fluxing agent were utilized which were A270 and a finer grind, Minex 7, from Indusmin Ltd. (product data sheets are presented in Appendix 2).

(iv) Spodumene :

a lithia aluminosilicate which is one of the most economical sources of lithia available to the ceramic industry. Spodumene is commonly used as a fluxing additive. This material was obtained from the Pottery Supply House located in Oakville, Ontario.

(v) Petalite :

another lithia aluminosilicate mineral which converts to beta spodumene upon heating. It has value as an auxiliary flux with feldspar and nepheline syenite. Petalite was also obtained from the Pottery Supply House.

ORT

(vi) Iron Oxide :

iron oxide is considered to be an excellent fluxing agent, disregarding the colouring effects produced by this material. A finely ground pigment grade of iron oxide, #628, was obtained from Norther Pigment in Toronto, Ontario.

(vii) Glass Cullet :

glass cullet refers to crushed or powdered waste glass. The cullet was obtained from Consumers Glass in Milton, Ontario in the form of ~1/4 inch chips. These chips were then ballmilled and the powdered glass screened to minus 150 mesh.

(viii) Commercial Glass Frit :

a lead-free glass frit was obtained from Ferro Industrial Products in Oakville, Ontario. This frit, #3110, is supplied to the brick industry as a body fluxing agent. The glass is high alkali, high borax and ground to minus 200 mesh. (Refer to Appendix 2).

(ix) Zinc Oxide :

zinc oxide is commonly used in the manufacture of glasses, glazes and enamels as a replacement flux for alkali constituents. A ceramic grade of zinc oxide, ZOCO 100, from the Zochem in Brampton, Ontario was used.

2.2 Preliminary Evaluation of Candidate Fluxing Agents

A series of small scale trial batches was prepared into which the candidate fluxing agents were substituted either individually or in combinations. Gradient firing trials were performed for each batch to identify the minimum firing temperature and compared to gradient firing results for clay only batches.

2.2.1 Batch Preparation

Each trial batch was prepared following a similar procedure. The batch formulations were made up to 1,000 grams (dry weight) in size and

mixed with approximately 1,000 grams of water in a high speed Waring Blendor for 10 minutes. The wet batch was then transferred to a beaker and stirred overnight to ensure a homogeneous mixture. Each batch was then poured onto plaster slabs and allowed to dry to a plastic body. The percent water of plasticity was determined for each batch at the point where the body could be freely peeled from the plaster slab. (Refer to Appendix 1 for tabulated values of lower plasticity limits). The dried batches were then manually extruded into 1/2" diameter rods using a push-rod hand extruder for gradient firing specimens.

2.2.2 Gradient Firings of Standard Clay Bodies

Gradient firing trials were performed for specimens from batches prepared with the existing Blue Mountain body formulations presented in Section 2.1 for reference purposes. Standard bodies based on the clays alone were also prepared for reference purposes. The formulations of these batches are presented in Table 1(i).

TABLE 1 (i)

Batch Formulations Based on Clays Only

Material	Weight Percent		
	Batch StB1	Batch StB3	Batch StB4
Red Clay	54	60	50
Green Clay	36	40	-
Blue Clay	10	-	50

The gradient firing results for these standard bodies are summarized in Table 1(ii). The specimens were qualitatively inspected for resistance to scratching of the surface with a sharp edge and porousness to the tip of the tongue to identify the lower temperature limits required for a well fired body.

TABLE 1 (ii)

Gradient Firing Results for Standard Clay Bodies

Batch	Min. Temp For Well Fired Body (^{o}C)	Comments
Bl. Mt. Slip casting body	~1000	-body porous to tongue up to 1020^{o}C firing
Bl. Mt. Pressing body	~1000	-body porous to tongue up to 1020^{o}C firing
StBl	~980	-porous to tongue up to 980^{o}C
StB3	~980	-porous to tongue up to 980^{o}C
StB4	~980	-porous to tongue up to 980^{o}C

The three batches prepared with the different clays only displayed firing properties which were quite similar. This could be expected since these clays originate from very similar shale deposits. The firing temperature of these clay-only bodies were found to be slightly lower than those of the two standard Blue Mountain bodies which is probably due to the presence of wollastonite in the Blue Mountain bodies.

2.2.3 Introduction of Candidate Fluxing Materials

2.2.3(a) Flyash, Silica Fume and Nepheline Syenite

The batch formulations containing flyash, silica fume and nepheline syenite are presented in Table 2(i).

TABLE 2 (i)

Batch Formulations with Additions of Flyash, Silica Fume and Nepheline Syenite

Material Added	Weight Percent of Material Added						
	SF1	SF2	SF3	SF6	SF7	SF8	SF11
Red clay	50.0	40	40	80	50	48	45
Green clay	-	25	25	-	-	32	45
Nepheline Syenite A270	10.0	-	-	10.0	10.0	-	-
Nepheline Syenite Minex 7	-	-	-	-	-	10	10
Wollastonite	-	-	-	-	-	10	-
Flyash	25.0	20	-	5.0	20.0	-	-
Silica Fume	15.0	-	20	5.0	10.0	-	-
Bell Dark Ball Clay	-	15	15	-	10.0	-	-

Upon preparing the first batch, SF1, it was found that the high levels of the very fine flyash and silica fume resulted in the body having very poor workability. Therefore ball clay was added to subsequent batches containing high levels of these two materials to improve the plasticity.

The gradient firing results for these batches are presented in Table 2(ii).

TABLE 2 (ii)

Summary of Gradient Firing Results for Batches
Prepared with Flyash, Silica Fume and Nepheline Syenite

Batch	Min. Temp For Well Fired Body (^{o}C)	Comments
SF1	~1010	-body porous to tongue up to 1040^{o}C firing
SF2	~1000	-body porous to tongue up to 1040^{o}C firing
SF3	~970	-body porous to tongue up to 1010^{o}C -specimens shattered after 1030^{o}C -multitude of white specks noticed throughout body
SF6	~1010	-body porous to tongue up to 1020^{o}C firing
SF7	~1010	-body porous to tongue up 1040^{o}C firing
SF8	~1000	-body porous to tongue up to 1020^{o}C firing
SF11	~1000	-body porous to tongue up to 1020^{o}C firing

From the results of this series of gradient firings no significant reductions in firing temperature were observed in any of the above batches in comparison to the clay-only bodies which appeared to be well fired at a temperature of about 980°C. (Refer to Section 2.2.1). The addition of flyash and nepheline syenite appeared to be increasing the firing temperature as the specimens from these batches were more porous at higher firing temperatures.

For this series of trials the lowest firing temperature of 970°C was observed with batch SF3 which contained 20% silica fume. This was not considered to be a significant reduction in comparison to the clay-only bodies. With this batch the fired specimens were observed to have a large number of white specks occurring throughout the body which probably originated from the silica fume. These specks were also observed in batches SF1 and SF7, containing 15 and 10% silica fume respectively, but to a lesser extent. The occurrence of these specks was considered to be undesirable with respect to appearance of the fired body.

2.2.3(b) Petalite and Spodumene

Trial batches were prepared with 10% addition levels of spodumene or petalite combined with 10% nepheline syenite Minex 7. An additional batch was prepared with 10% spodumene only substituted into the clay body. The formulation for these batches are presented in Table 3(i).

TABLE 3 (i)

Batch Formulations Containing Neph.Syen.Minex 7 Spodumene and Petalite

Material	Weight % SF10	SF12	SF13
Red Clay	40	40	45
Blue Clay	40	40	45
Neph.Syen.Minex 7	10	10	-
Petalite	-	10	-
Spodumene	10	-	10

The summary of the gradient firing for these three batches is presented in Table 3(ii).

TABLE 3 (ii)

Summary of Gradient Firings for Batches Prepared with Petalite and Spodumene

Batch	Min. Temp For Well Fired Body (^{o}C)	Comments
SF10	~980	-body porous to tongue up to 1000^{o}C
SF12	~980	-body not porous to tongue after 980^{o}C
SF13	~960	-body not porous to tongue after 980^{o}C

From these gradient firing trials it was found that the addition of 10% spodumene slightly reduced the firing temperature of the clay body to 960^{o}C but not to the desired temperature range. Comparison of the fired limits for batches SF10 and SF13 of 980 and 960^{o}C indicate that the nepheline syenite present in SF10 is not contributing to the fluxing of the body at these temperatures since batch SF13 containing spodumene only has the lower firing temperature.

2.2.3(c) Glass Cullet, Ferro Frit 3110 and Iron Oxide

A series of batches containing additions of these materials was prepared. The batch formulations are presented in Table 4(i).

ORF

TABLE 4 (i)

Batch Formulations Containing Glass Cullet
Ferro Frit 3110 and Iron Oxide Pigment

Material	Weight %				
	SF4	SF14	SF15	SF16	SF17
Red Clay	48.5	45	40	40	40
Blue Clay	32.5	45	40	40	40
Green Clay	9	-	-	-	-
Iron Oxide	-	10	10	-	-
Glass Cullet	10	-	10	20	-
Ferro 3110	-	-	-	-	20

The gradient firing results are summarized in Table 4(ii).

The results of this series of gradient firings proved to be the most promising. Initially it was found that a 10% addition of glass cullet (-150 mesh) to the clay body reduced the firing temperature of the body to as low as 875°C. To further reduce the firing temperature the level of glass cullet was increased to 20% in batch SF16 which provided a firing temperature as low as 840°C. The specimens fired near 840°C were difficult to scratch with a sharp edge and were not porous to the tongue. Specimens from all of the other batches listed previously fired near this temperature were easily gouged with a sharp edge and in many cases crumbled.

ORF

TABLE 4 (ii)

Summary of Gradient Firings for Batches Prepared with Iron Oxide, Glass Cullet and Ferro Frit 3110

Batch	Min. Temp For Well Fired Body (^{o}C)	Comments
SF4	~875	-body not porous to tongue after 900^{o}C
SF14	~940	-body not porous to tongue after 940^{o}C -body colour darkened considerably
SF15	~900	-body not porous to tongue after 900^{o}C -body colour darkened considerably
SF16	~840	-body not porous to tongue after 850^{o}C
SF17	~840	-same as SF16

ORI

Similar promising results were obtained with 20% addition of a commercial glass frit, Ferro frit 3110, which was recommended by Ferro Industrial Products for use as a body flux. Again the firing temperature of the clay body was reduced to near 840°C.

The addition of iron oxide was also found to reduce the firing temperature of the clay body in batch SF14 but not to the extent of the glass cullet. The colour of the body was darkened to a deep rich brown which was considered to be a pleasant colour.

2.2.3(d) Zinc Oxide and Titanium Dioxide

Trial batches were prepared with varying levels of zinc oxide and titanium dioxide. These formulations are presented in Table 5(i). The gradient firing trial summaries are presented in Table 5(ii).

TABLE 5 (i)

Batch Formulations Containing Zinc Oxide Titanium Dioxide and Glass Cullet

Material	Weight %					
	SF18	SF19	SF20	SF21	SF22	SF23
Red Clay	45	40	40	45	54	51
Blue Clay	45	40	40	45	-	-
Green Clay	-	-	-	-	36	34
ZnO	10	10	10	-	5	5
TiO_2	-	-	10	10	5	-
Glass Cullet	-	10	-	-	-	10

ORF

TABLE 5 (ii)

Summary of Gradient Firing Trials for Batches Prepared with Zinc Oxide and Titanium Dioxide

Batch	Min. Temp For Well Fired Body (^{o}C)	Comments
SF18	~1020	-porous to tongue up to 1040^{o}C -body is light tan colour between 875 and 1020^{o}C -colour darkens after 1040^{o}C; glossy surface starting after 1070^{o}C
SF19	~950	-porous to tongue up to 970^{o}C -body is light tan colour between 870 and 1020^{o}C; slightly darker than batch SF18
SF20	~970	-porous to tongue up to 970^{o}C -body is light tan between 825 and 1060^{o}C; body is lighter colour than SF18 or SF19 -darkening of colour after 1060^{o}C; glossy surface after 1060^{o}C
SF21	~970	-porous to tongue up to 980^{o}C -body is pink up to 1020^{o}C and becomes tan; colour is darker than SF18 up to 1060^{o}C -no glossiness

ORI

Table 5 (ii) continued

Batch	Min. Temp For Well Fired Body (^{o}C)	Comments
SF22	~970	-porous to tongue up to 980^{o}C -body is pink up to 930^{o}C and becomes tan; colour is similar to batch SF20 after 1000^{o}C only slightly darker
SF23	~950	-porous to tongue up to 950^{o}C -body is tan colour after 900^{o}C; slightly darker than all earlier batches containing ZnO

Initially the zinc oxide was added to batch SF18 at a 10% level as a candidate fluxing agent. Examination of the gradient firing results reveals that the zinc oxide did not prove to be a satisfactory fluxing agent, however, it was found that the zinc oxide produced a change in the colour of the body. The normal terra cotta colour was altered to a light tan colour over the firing range of 875 to 1,020^{o}C after which the colour began to darken. In batch SF20 10% titanium dioxide was added in combination with 10% zinc oxide in an attempt to further lighten the body colour. The colour of this batch proved to be very light tan over the temperature range of 825 to 1060^{o}C (see Figure 1). Batch SF22 was prepared with 5% zinc oxide and 5% titanium dioxide. The tan colour produced was similar to batch SF18 containing 10% zinc oxide only and slightly darker than that of batch SF20.

ORF

Batches SF19 and SF23 were prepared with 10% additions of glass cullet combined with additions of 10 and 5% of zinc oxide respectively. The firing temperatures of these two batches proved to be higher than expected at about 950°C for each. The glass cullet was less effective in its fluxing action for these batches which was believed to be due to the presence of the zinc oxide.

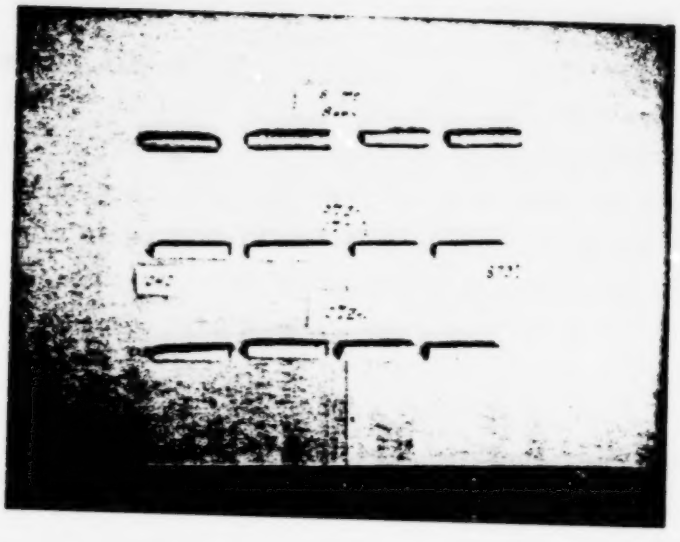

Figure 1

Comparison of Body Colour of Gradient Samples from Batch SF20 (10% ZnO, 10% TiO2) Batch SF18 (10% ZnO) and Existing Blue Mountain Body

2.3 Evaluation of Most Promising Batches

Upon reviewing the results of the gradient firing trials the most promising body formulations were selected for further evaluation. These batches included batch SF16 and SF17 containing 20% glass cullet and 20% Ferro frit 3110 respectively. Two additional batches were evaluated as well. Batch SF25 was prepared with substitutions of 20% glass cullet and

10% zinc oxide into the clay body. Batch SF27 was prepared with an addition of 10% Ferro frit 3110 only. The properties of these trial batches were compared to those of a batch with the Blue Mountain pressing body formulation prepared under similar conditions.

Each of these batches was prepared by mixing 10 kilograms (dry weight) of the body formulation and 8 kilograms of water with a high speed Lightnin mixer overnight. The wet batches were dried on plaster slabs. The dried batches were then pugmilled and extruded using a Rawdon de-airing extruder. Specimens with the dimensions of 1"x3/4"x6" were extruded for evaluation with respect to strength, moisture absorption, shrinkage and shape stability during firing at three temperatures of 850, 950 and 1050°C.

2.3.1 Strength Evaluation

The modulus of rupture was determined for specimens from each batch with an Instron compresive strength testing instrument equiped with a three-point-bending rig. The specimens were loaded with a crosshead rate of 0.05 inches/minute and a span of 5 inches between the supporting pins. A minimum of 8 specimens was used to determine each average modulus of rupture value. These values are presented in Table 6.

TABLE 6

Average MOR's for Unfired and Fired Specimens

Batch	Percent H_2O After Extrusion	Dry Unfired	Average MOR (psi) 850°C	950°C	1050°C
SF16 - 20% glass cullet	14.69	404±27	4053±241	3578±509	4556±443
SF17 - 20% Ferro 3110	13.56	377±38	3807±281	3422±125	3886±597
SF25 - 20% glass 10% ZnO	15.38	381±13	3154±342	3780±366	4797±389
SF27 - 10% Ferro 3110	14.12	386±58	3684±410	3691±588	4139±476
B.M. Press Body	17.65	246±14	2108±426	3542±232	3882±330

ORF

The dry unfired strengths of all of the batches containing either the glass cullet or glass frit are higher than that of the Blue Mountain body. This may be due to the larger particle size of the glassy materials providing better particle packing with the finer clays.

With respect to fired strength, batch SF16 containing 20% glass cullet proved to have the highest strength of the batches fired at 850°C and was almost double that of the Blue Mountain body fired at 850°C. In fact, batch SF16 was significantly stronger fired at 850°C than the Blue Moiuntain body fired at 1050°C. The next highest strengths at 850°C were produced by batch SF17 containing 20% Ferro frit 3110 and these specimens proved to be equally as strong as the Blue Mountain body fired at 1050°C.

Batch SF25 prepared with 20% glass cullet and 10% zinc oxide was observed to have the lowest strengths of the trial batches fired at 850°C but were still 50% stronger than the Blue Mountain body fired at this temperature. Again the zinc oxide has had some effect on the fluxing action of the glass cullet as was noted previously in Section 2.2.3(d).

Examination of the strengths of the batches when fired at 950°C reveals that the batches have practically equivalent strengths including the Blue Mountain body. Both batches SF16 and SF17 had dropped in strength. An explanation for this is that at 850°C the glass may not be completely molten but softens to the extent that it forms a cement like bond between the clay particles. At higher temperatures the glass is more fluid and will flow over the entire surface of the particles thus leaving a narrower cemented zone between the particles. Also the more fluid glass may be migrating to the centre of the specimens as indicated in a number of specimens having developed black cores after firing to 950°C.

When fired to 1050°C the strongest specimens were produced from batch SF25. The strong fluxing action of zinc oxide at this temperature was evident as the specimens showed signs of melting and some specimens fused

together. The strengths of all of the other trial batches were slightly higher than or equivalent to the Blue Mountain specimens.

The colour of batch SF25 was observed to be lightest when fired at 950°C and was more of a sand colour than the tan colour observed in the gradient firings. This was felt to be due to the higher level of glass cullet added to this batch. The colour had darkened considerably at 1050°C. When fired at 850°C the terra cotta colour was still evident as the body was a pale orange colour.

In batches SF17 and SF27, both containing Ferro frit 3110, it was found that a small number of specimens split completely along the length of the bar. Two specimens out of 10 from batch SF17 and one from batch SF27 split when fired at 950°C. At 1050°C one specimen split from each batch. This may have been due to incomplete drying before firing, or some form of stress that has developed during firing.

2.3.2 Moisture Absorption

The percentage moisture absorption for each batch was determined by boiling pre-weighed bars in a water bath for two hours and then reweighing the bars after sponging off the surface water. The percentage weight increase after boiling was then calculated and the values are presented in Table 7.

ORE

TABLE 7

Percent Moisture Absorption

Batch	Average % Absorption		
	850°C	950°C	1050°C
SF16 - 20% glass cullet	8.9	7.0	1.2
SF17 - 20% Ferro 3110	4.8	2.3	2.9
SF25 - 20% glass cullet 10% ZnO	9.5	6.2	0.2
SF27 - 10% Ferro 3110	8.0	4.4	3.7
B.M. Press Body	15.8	14.0	12.3

The lowest water absorption at 850°C was observed in the specimens prepared with 20% Ferro frit (SF17). Significant reductions of water absorption, in relation to the Blue Mountain press body, were observed in all of the trial batches fired at 850°C. The absorptions for specimens from all of the trial batches fired at 850°C were even lower than that of the Blue Mountain body fired at 1050°C.

The percentage absorption for specimens prepared from batch SF25 fired at 850°C was slightly higher than batch SF16 but at 950°C the value was lower in batch SF25 indicating the additional fluxing action of the zinc oxide at 950°C. Specimens fired at 1050°C showed almost no water absorption for batch SF25 indicating that this body is almost completely vitrified.

2.3.3 Firing Shrinkage

The percentage linear shrinkage was determined for specimens from each batch fired at 850, 950 and 1050°C. These values are presented in Table 8.

TABLE 8

Average Percent Linear Shrinkage Values

Batch	Average % Shrinkage (5 specimens)		
	850°C	950°C	1050°C
SF16	2.01	2.20	2.72
SF17	2.16	2.53	2.61
SF25	1.88	2.47	Specimens Deformed
SF27	0.72	1.88	2.33
B.M. Press Body	0.21	0.60	0.95

The lowest shrinkage was observed in the specimens from the standard Blue Mountain press body at all three firing temperatures. The shrinkages of specimens from batches SF16 and SF17 were significantly higher than the standard body when fired at 850°C as well as at the higher temperatures. This is partially due to the presence of Wollastonite in the Blue Mountain body since wollastonite reduces fired shrinkage.

The specimens from batch SF25 deformed at 1050°C, therefore, the shrinkage values were neglected.

2.3.4 Slump Tests During Firing

Specimens from each batch were placed on supporting posts which were 5" apart in the kiln and a load of 350 grams was centrally placed on each specimen as illustrated in Figure 2. The specimens were then fired at 850°C and 1050°C and the deflection of the specimen measured. This was merely a qualitative test to determine if the shape of the specimen would be stable at these firing temperatures. The measured deflections for these specimens are presented in Table 9.

TABLE 9

Deflections of Weighted Specimens During Firing

Batch	Deflection (millimeters)	
	850°C	1050°C
SF16	0.61	none detected
SF17	0.58	0.71
SF25	none detected	7.82
SF27	none detected	none detected
B.M. Press Body	0.83	0.68

For the specimens fired at 850°C there was no significant slumping observed. At 1050°C the specimen from batch SF25 was observed to have slumped considerably during firing which indicated that these specimens were melting at this temperature due to the fluxing action of the zinc oxide and glass cullet combined.

The specimen from batch 27 containing 10% Ferro frit was found to have split into two clean sections along its length as shown in Figure 2. The specimens were well dried before firing therefore some form of stress has developed within the body.

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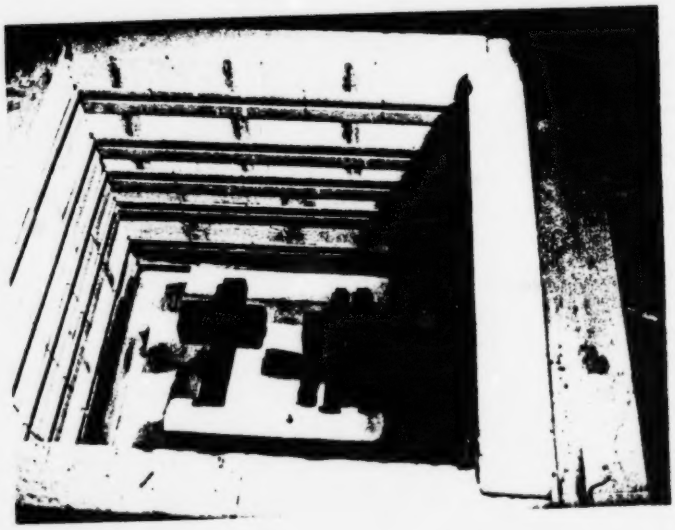

Figure 2

Photograph of Slump Tests to Determine Shape Stability During Firing
Specimen above from batch SF27 has split due to internal stress.

3. BATCH PREPARATION FOR PLANT TRIALS

One of the most promising body formulations was selected by Blue Mountain for evaluation in plant trials. The batch selected was SF17 containing 20% Ferro frit 3110. 10% wollastonite and 3% nepheline syenite were also added to simulate the Blue Mountain pressing body formulation.

A 20 kilogram (dry weight) batch was prepared by mixing the raw materials and 20 kilograms of water with a high speed Lightnin mixer. The batch was allowed to stir overnight. The slurry was then filterpressed at a pressure of 90 psi into 1 foot square filter cakes. The filter cakes were then pugmilled in the Rawdon extruder and extruded at a de-airing pressure of 29 psi into 3 inch diameter slugs about 8 inches in length.

The consistency of the batch was found to be very firm after a period of about 1/2 hour from extruding. The moisture content was determined and found to be 13.4% which was quite low compared to the moisture content required by Blue Mountain of approximately 20%. The amount of water needed to bring the moisture content to 20% was calculated and the additional water mixed with the body in the pugmill, allowing the batch to pass through several times to ensure proper mixing. The consistency of the body was quite pliable prior to extruding. Upon extruding the body again became very stiff after standing (under plastic cover) for about 1/2 hour. The moisture content proved to be only 14.3%.

The procedure of pugmilling with additional water was repeated. In this case a considerable amount of excess water was added while pugmilling. The consistency of the batch became so pliable that the material would not travel through the auger and push out the remainder already in the auger. By applying almost constant manual pressure at the auger feed it was possible to force the material through the pugmill until it was well mixed. The consistency of the de-aired extruded batch seemed quite pliable immediately after extrusion but within an hour the batch had stiffened considerably. Again the moisture content was found to be too low at 15.3%.

The presence of the high level of the glass frit is hindering the body in retaining the water and thus the batch is drying rapidly. Initially the filter cakes must have dried rapidly as they were left overnight, covered with plastic, prior to extruding. Also, when it was found that the moisture level was too low after extruding, the body may not have been allowed to open up enough when pugmilled with the addition of water which resulted in the very low increase in moisture content after repeatedly mixing with more water.

This batch was not used by Blue Mountain for pressing trials to avoid damaging the pressing moulds and was scrapped. Plant trials were performed with an alternative experimental batch which was prepared at Blue Mountain. For this batch 10% zinc oxide was added directly to the Blue Mountain casting slip. The decalling trials for this batch are discussed in the Blue Mountain report.

4. CONCLUSIONS AND RECOMMENDATIONS

Based on the results obtained throughout the course of the experimental work performed at ORF, the following conclusions and recommendations can be made.

(i) The addition of 20% glass cullet or Ferro frit 3110 to bodies based on the clays utilized by Blue Mountain Pottery produced a well fired body at firing temperatures as low as 840^{o}C.

(ii) The strengths and moisture absorption of batches containing a 20% level of glass cullet and Ferro frit 3110 and fired to 850^{o}C were significantly improved in comparison to the existing Blue Mountain pressing body fired as high as 1050^{o}C. The batch prepared with the combination of 20% glass cullet and 10% zinc oxide also displayed significant improvements in moisture absorption when fired at 850^{o}C with reasonable fired strength.

(iii) The addition of 10% zinc oxide to the Blue Mountain clay body causes a change in colour of the body from terra cotta to a light tan. The further addition of 10% titanium dioxide lightens the colour more and over a broader firing range.

(iv) The presence of a 20% level of glassy material in the clay body causes the body to be less pliable upon extruding. This is probably due to the batch drying quickly since the glass will not adsorb moisture as readily as the clay materials. It may be necessary to reduce the level of non-clay materials in the formulation and increase the clay level to improve the plasticity of the extruded body. Using a finer ground glass cullet or frit should allow lower levels of this fluxing agent to be used.

(v) Further developmental work is required in order to optimize the levels of the substitute fluxing agents in the clay body and to develop the production technology required to produce these body formulations at a commercial level.

S. Johar, Manager

J. Foster

Materials Division
Glass and Ceramics Centre

ORF

APPENDIX 1

Lower Limits of Plasticity of Trial Batches

ORF

Lower Limits of Plasticity of Trial Batches

Batch I.D.	Criterion (percent)	Percent H_2O of Plasticity
Bl.Mt. Slip casting body	-	18.66
Bl.Mt. Pressing body	-	18.48
St Bl	54 red clay 36 green clay 10 blue clay	20.06
St B3	60 red clay 40 green clay	21.35
ST B4	50 red clay 50 blue clay	19.15
SF 1	10 neph.syen. A270 25 flyash 15 silica fume	24.15
SF 2	20 flyash 15 ball clay	21.83
SF 3	20 silica fume 15 ball clay	25.05
SF 6	10 neph.syen. A270 5 flyash 5 silica fume	22.34
SF 7	10 neph.syen. A270 20 flyash 10 silica fume 10 ball clay	25.2
SF 8	10 neph.syen. Minex 7 10 wollastonite	19.40
SF 11	10 neph.syen. Minex 7	18.39
SF 10	10 neph.syen. Minex 7 10 spodumene	18.57
SF 12	10 neph.syen. Minex 7 10 petalite	18.26

ORI

(continued)

Lower Limits of Plasticity of Trial Batches

Batch I.D.	Criterion (percent)	Percent H_2O of Plasticity
SF 13	10 spodumene	19.59
SF 4	10 glass cullet	18.31
SF 14	10 iron oxide	18.72
SF 15	10 iron oxide 10 glass cullet	18.45
SF 16	20 glass cullet	16.36
SF 17	20 Ferro 3110	18.84
SF 18	10 ZnO	19.52
SF 19	10 ZnO 10 glass cullet	19.10
SF 20	10 ZnO 10 TiO_2	21.08
SF 21	10 TiO_2	20.63
SF 22	5 ZnO 5 TiO_2	21.59
SF 23	5 ZnO 10 glass cullet	18.08

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APPENDIX 2

Supplier's Raw Material Specifications

INDUSMIN SYENITE

Nepheline Syenite Products

Used extensively in the ceramic whitewares industry are Grades A-200, A-270 and A-400. These are differentiated by their fineness of grind and particle size distribution which bear definite relationships to their fluxing characteristics. Figure 1 compares the relative fusibility of Grades A-200, A-270 and A-400.

In designing ceramic bodies, it is important to consider the difference in fluxing activity of the various grinds of Nepheline Syenite as well as the difference in fluxing activity between these products and feldspar. Figure 2 is a rough guide of the relative amounts of Nepheline Syenite products required to provide fluxing action equal to a typical 200-mesh pottery grade feldspar.

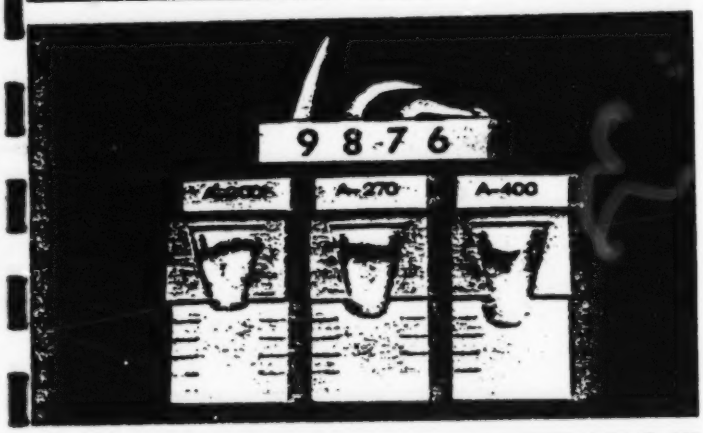


FIG. 1

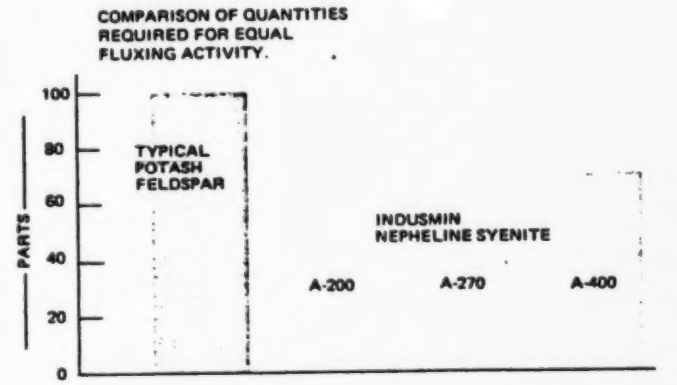


FIG. 2

Supply

Unlimited from conveniently located mine and plant at Nephton, Ontario near Peterborough. Direct rail and transport routes assure efficient distribution in bulk or in convenient multi-wall bags.

Technical Centre

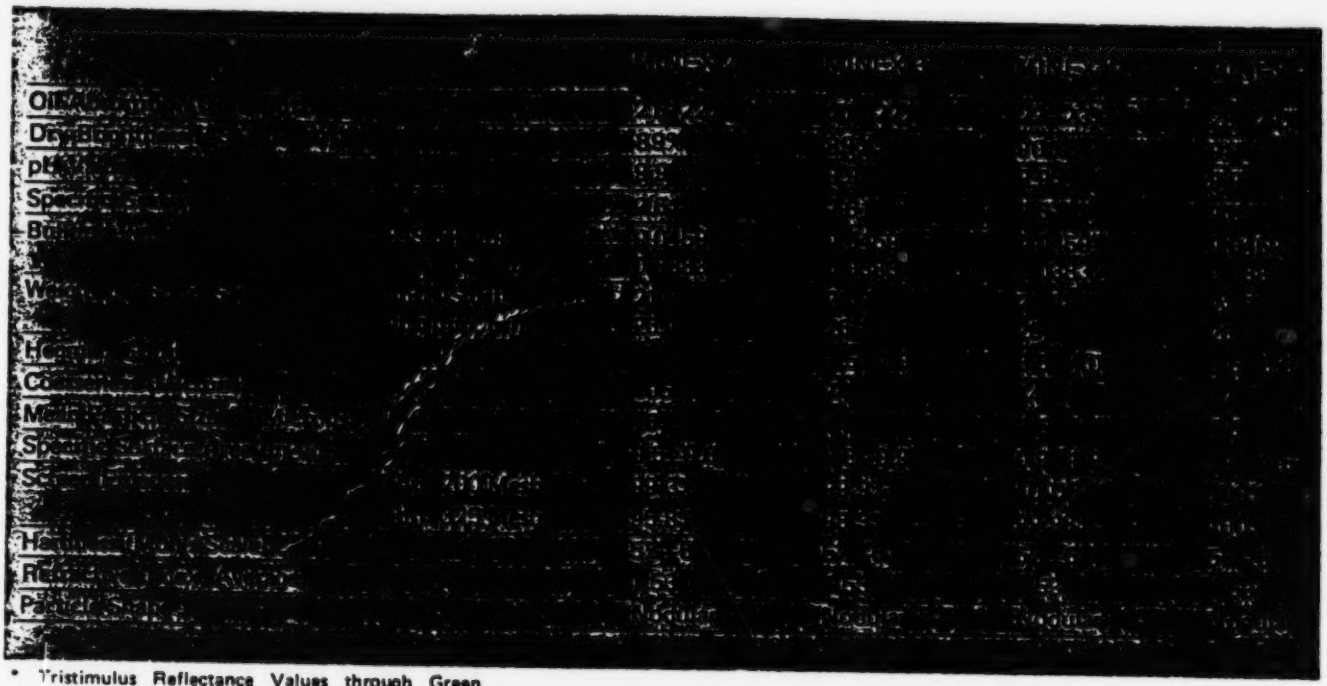
Our competent professional staff is ready to provide assistance with your technical problems at no obligation. Our completely equipped Technical Centre carries on a continuous development program and an extensive library of proven application data has been compiled.

The following are typical data on the Nepheline Syenite products for ceramic applications.

Typical Chemical Analysis	%
SiO_2	60.7
Al_2O_3	23.3
Fe_2O_3	0.07
CaO	0.7
MgO	0.1
Na_2O	9.8
K_2O	4.6
L.O.I.	0.7

Physical	A200	A270	A400
% Finer than 325 mesh	95	98	100
% Finer than 10 microns	33	42	65
Pyrometric Cone Equiv.	6	5	3
pH	9.8	9.9	9.9

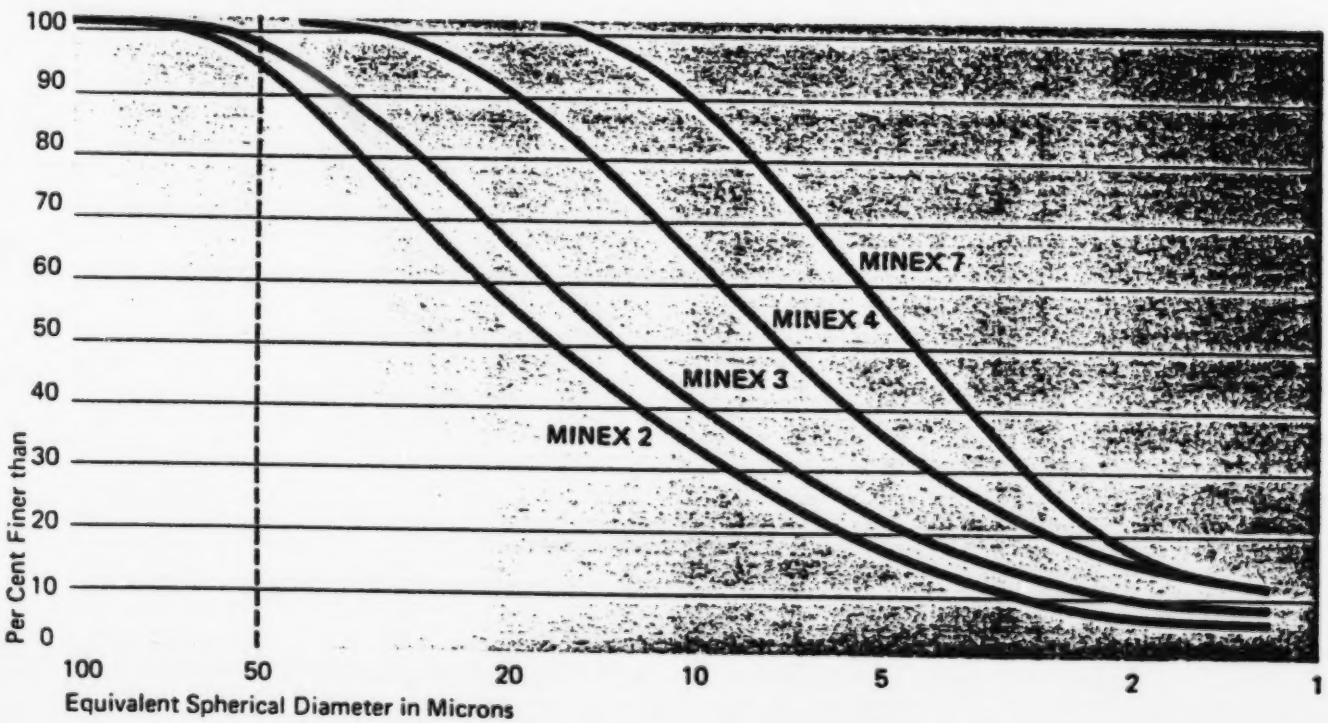
Physical Properties



* Tristimulus Reflectance Values through Green Filter of Zeiss Elrepho Unit, CIE standard Illuminant C.

** As determined by Sedimentation Method, i.e. the 50% point on the particle size distribution curve.

Particle Size Distribution



THE POTTERY SUPPLY HOUSE LIMITED

P. O. Box 192 • 2070 SPEERS ROAD, OAKVILLE, ONTARIO • (416) 827-1129

PERCENTAGE COMPOSITION - CHEMICAL ANALYSIS

MATERIAL	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	B_2O_3	Li_2O	P_2O_5
Whiting	---	---	0.1	----	98.2	0.3	---	0.5	---	----	---
Dolomite	---	0.3	0.8	---	54.8	44.0	---	---	---	---	---
Wollastonite	50.9	0.3	0.8	---	46.9	0.1	---	---	---	---	---
Colemanite Gerst. Borate	9.5	1.1	0.3	---	15.9	3.5	---	4.9	33.0	---	---
Bone Ash	---	0.5	0.1	---	53.9	1.3	---	---	---	---	40.9
Magnesium Carbonate						42.3					
#Y Talc	56.6	0.3	---	---	8.0	29.2	---	---	---	---	---
Magnesium Oxide	---	0.1	---	---	1.4	98.5	---	---	---	---	---
Lithium Carb.										40.4	---
Amblygonite	1.4	34.4	0.2	---	0.2	---	0.3	1.6	---	8.4	---
Lepidolite	53.5	26.0	---	---	---	---	11.5	0.3	---	4.2	---
Petalite	76.1	17.3	---	---	---	---	0.6	---	---	4.3	---
Spodumene	64.1	26.4	0.6	---	0.3	---	0.3	0.3	---	7.1	---
Aplite	80.6	24.1	0.2	---	5.7	---	2.5	6.3	---	---	---
Plastic Vitrox	75.6	14.8	---	---	0.2	0.2	6.8	0.3	---	---	---
Kyanite	41.0	60.4									
Pyrophyllite	75.4	20.3	0.1	---	0.2	---	---	0.2	---	---	---
Alumina Hydrate	0.1	64.0	---	---	---	---	---	0.7	---	---	---

NOTE: The above information is believed to be factual but is only as correct as the source from which it is taken.

CERAMIC CONSULTANTS

NORTHERN PIGMENT

TYPICAL PHYSICAL and CHEMICAL CHARACTERISTICS

NORTHERN PIGMENT IRON OXIDES

Colour Number	Iron Oxide Content % Fe_2O_3	Hydrated Iron Oxide Content $Fe_2O_3 \cdot H_2O$	Water Soluble Salts %	Acid Insoluble %	Oil Absorption ASTM	Residue 325 Mesh	Specific Gravity	U.S. Gal. Bulk Lbs. per Gal.	Hiding Sq. Ft./Lb.	Particle Shape
300	—	99.5	0.5	Trace	50-60	0.1-0.5	4.05	33.74	400	
305	—	99.5	0.5	"	50-60	0.1-0.5	4.05	33.74	400	
307	—	99.5	0.5	"	50-60	0.1-0.5	4.05	33.74	400	Acicular
310	—	99.5	0.5	"	50-60	0.1-0.5	4.10	34.15	375	
315	—	99.5	0.5	"	50-60	0.1-0.5	4.10	34.15	375	
3100	—	99.5	0.5	"	40-45	0.1-0.5	4.05	33.74	400	
3105	—	99.5	0.5	"	40-45	0.1-0.5	4.05	33.74	400	Acicular
401	99.5	—	0.4	"	30-40	0.1-0.5	4.75	39.98	1000	
403	99.5	—	0.4	"	30-40	0.1-0.5	4.80	39.98	1000	
404	99.5	—	0.4	"	30-40	0.1-0.5	4.80	39.98	1000	
405	99.5	—	0.35	"	30-40	0.1-0.5	4.80	39.98	1000	
407	99.5	—	0.35	"	30-40	0.1-0.5	4.80	39.98	1000	Acicular
408	99.5	—	0.2	"	30-40	0.1-0.5	4.85	40.40	900	
409	99.5	—	0.2	"	30-40	0.1-0.5	4.85	40.40	900	
522	99.5	—	0.2	"	20-30	0.1-0.5	4.90	40.82	850	
533	99.5	—	0.2	"	20-30	0.1-0.5	4.90	40.82	850	
4110	97.0	—	0.2	"	30-40	0.1-0.5	5.0	41.8	1000	
4120	97.0	—	0.2	"	30-40	0.1-0.5	5.0	41.8	1000	Spherical
4130	97.0	—	0.2	"	30-40	0.1-0.5	5.0	41.8	1000	
6406	95.0	—	0.2	3.5	20-30	0.1-1.0	4.95	41.23	700	Acicular and Cubic
114	96.0	—	0.40	1.0		0.1-1.0	4.45	37.07		
118	96.0	—	0.40	1.0		0.1-1.0	4.45	37.07		
132	93.5	—	0.40	0.5		0.1-1.0	4.30	35.82		Acicular and Cubic
175	96.0	—	0.40	0.5		0.1-1.0	4.30	35.82		
177	96.0	—	0.40	0.5		0.1-1.0	4.30	35.82		
604	96.0-97.0	—	0.4	2-3	31	0.1	4.70	39.15		
608	96.0-97.0	—	0.4	2-3		0.1	4.65	38.63		Cubic
628	96.0-97.0	—	0.4	2-3		Nil		38.63		
1511	55-60	—	0.5	14-16	57	0.1-1.0	3.66	30.05		
1616	50-60	—	0.5	14-16	43	0.1-1.0	3.59	29.82		Amorphous

FERRO LEADLESS GLAZE FRITS — PERCENTAGE COMPOSITIONS

Frit No.	Coeff. of Exp.	K_2O	Na_2O	Li_2O	CaO	MgO	BaO	SrO	ZnO	Al_2O_3	B_2O_3	SiO_2	ZrO_2	F	
3271	9.3	—	12.8	—	11.0	—	—	—	—	—	21.6	54.6	—	—	
3289	8.2	—	5.5	—	—	—	27.4	—	—	5.4	12.4	49.3	—	—	
3270	9.4	5.5	8.6	—	9.4	—	—	—	—	8.6	16.5	51.4	—	—	
3134	9.6	—	10.3	—	20.1	—	—	—	—	—	23.1	46.5	—	—	
3814	8.9	0.4	8.7	—	16.8	—	—	—	—	5.0	19.3	49.8	—	—	
3124	7.9	0.7	6.3	—	14.1	—	—	—	—	9.9	13.7	55.3	—	—	
5301	11.6	5.1	19.2	—	2.3	—	—	—	—	11.3	11.7	41.8	—	8.6	
3286	7.5	3.4	1.7	—	11.2	—	—	8.6	—	6.2	8.8	60.1	—	—	
3240	8.6	0.6	4.5	—	8.8	—	7.9	—	15.8	0.9	9.9	39.5	10.2	1.9	
3248	6.8	7.0	1.6	—	5.2	2.0	—	—	—	15.1	4.7	64.4	—	—	
3820	9.2	8.1	5.1	—	5.3	0.5	—	—	9.6	13.0	4.6	50.9	2.9	—	
3110	10.1	2.3	15.3	—	6.3	—	—	—	—	3.7	2.6	69.8	—	—	
3247	8.6	—	—	—	—	—	53.1	—	—	5.3	—	41.6	—	—	
3831	11.9	12.0	4.6	—	12.2	—	17.9	—	—	10.6	—	42.7	—	—	
3851	4.2	—	—	—	0.5	23.8	—	—	—	26.8	—	48.9	—	—	